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$^{17}O^{18}O$ and $^{18}O^{18}O$ in firn air O_2 from East Greenland and Antarctica

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Abundances of $^{17}O^{18}O$ and $^{18}O^{18}O$ (called clumped isotopes, denoted by Δ_{35} and Δ_{36}) of O_2 in polar firn and ice core air can be useful to study past changes in atmospheric photochemistry. We present Δ_{35} and Δ_{36} values measured in firn air O_2 from East Greenland (EGRIP: 75.63ºN, 35.99ºW) and EPICA Dome C, Antarctica (75.10 ºS, 123.33 ºE). Firn air samples were collected down to the bubble close-off depth. The mean age of the firn air increases with depth to ∼40 and ∼50 years at close-off at EGRIP and Dome C, respectively. Measurements of Δ_{35} and Δ_{36} were carried out using a high-resolution stable isotope ratio mass spectrometer Themro Fisher 253 ULTRA at medium mass resolution (mass resolving power ∼10000). We demonstrated that 253 ULTRA can resolve all the major isobaric interferences for O_2 clumped isotope measurements such as the influence of ^{35}Cl (mass 34.9688 u) on $^{17}O^{18}O$ (mass 34.9983) and $H^{36}Cl$ (mass 35.9767 u) and ^{36}Ar (mass 35.9675 u) on $^{18}O^{18}O$ (mass 35.9983). Thus the two clumped isotope species of O_2 can be measured without correction even if the O_2 samples are not fully free from these potential isobars (Laskar et al., 2019). The isotopic effect due to gravitational settling is insignificant for the second order isotope signatures Δ_{35} and Δ_{36}, although strongly affects the conventional isotope ratios. The average Δ_{35} and Δ_{36} values for the Dome C firn air O_2 are 1.26±0.06 ‰ and 2.42±0.10 ‰ respectively. For the EGRIP, the values are 1.28±0.09 ‰ and 2.40±0.10 ‰ respectively. No significant difference in the Δ_{35} and Δ_{36} values with depth are observed indicating that potential temporal trends in the clumped isotope signatures of O_2 are below the present measurement precision. In order to estimate the expected temporal variation, we simulated the temporal evolution of Δ_{36} from 1960 to 2010 using the European Centre for Medium-Range Weather Forecasts – Hamburg (ECHAM)/Modular Earth Submodel System (MESSy) Atmospheric Chemistry (EMAC) model. The model results confirm that expected changes in Δ_{36} over this period are indeed smaller than the present analytical precision. The modeled Δ_{36} values agree well with the measurements. We plan to extend the measurements and model simulations to study glacial-interglacial variation in the atmospheric photochemistry and tropospheric temperature using Δ_{35} and Δ_{36} values in O_2 trapped in polar ice core air with enhanced analytical precision.

References

Laskar A. H., Peethambaran, R., Adnew, G. A. and Röckmann, T. (2019) Measurement of $^{18}O^{18}O$ and $^{17}O^{18}O$ in atmospheric O_2 using the 253 Ultra mass spectrometer and applications to stratospheric and tropospheric air samples. Rapid Comm. Mass Spec. (under review)